The Coupled Electro-Mechanical Behaviour of Nanocomposites

J.M. Wernik, W.S. Bao and S.A. Meguid

Mechanis and Aerospace Design Laboratory, Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario, M5S 3G8, Canada

ABSTRACT

In this research, we intend to introduce multifunctionality into epoxy adhesives through the homogeneous dispersion of carbon nanotubes. Specifically, we are interested in improving the mechanical properties and electrical conductivity of the adhesive. The increased electrical conductivity would facilitate the use of the embedded nanofillers for sensing in situ local damage, thus allowing the quantitative in-flight self-health monitoring of structural adhesive bonds. In this presentation, we will outline the progress made so far and the challenges we are facing. Specifically, we will address the first phase in which the authors have developed numerical models to study the behavior of carbon nanotubes, nanoreinforced interfaces and the tailoring of mechanical and electrical properties.

Keywords: multifunctional, nanocomposite, health montoring, carbon nanotube, structural adhesive bonds

1 INTRODUCTION

In the past two decades, practical realisation of composites began to shift from microscale-reinforced composites to nano-reinforced composites using carbon nanotubes (CNTs). There are a number of advantages that result from dispersing CNTs into polymeric materials. For example, whereas traditional composites can use over 40 wt % of the reinforcing phase, the dispersion of just 0.1 wt% of CNTs into a polymeric matrix could lead to dramatic changes in their mechanical and electrical properties, leading to added functionalities. Due to this unique combination of physical and mechanical properties, CNTs have emerged as excellent candidates for use as tailoring agents of polymeric materials. They will yield the next generation multifunctional nanocomposites for use in a variety of applications; including primary transport structures, smart coatings, lightening strike protection for aircraft, housings for cell phones/computers, to name a few.

In this work, we present a numerical technique which can be used to predict the strain-conductivity relationship for a nanocomposite containing CNTs. We combine the atomistic-based continuum (ABC) multiscale modeling technique with micromechanical methods to predict the effective mechanical properties of the nanocomposite (Fig.1). Here a three-dimensional nonlinear representative volume element (RVE) is used as the fundamental building block of the nanocomposite system. The RVE is in turn used with appropriate micromechanical modeling methods to scale up to the macro level and predict the bulk mechanical properties. The electrical conductivity is predicted via an equivalent resistor network model developed using Monte Carlo simulations (Fig,2). The constitutive laws which govern electron tunneling are formulated on the basis of the landauer-Buttiker formula while the intrinsic conductivity is accounted for through the Drude model.

In this presentation, we will report some of our preliminary results and identify the challenges that we are facing. Specifically, we present the results of our ABC modeling and micromechanical analysis and discuss the effects of such processing parameters as CNT alignment, concentration and aspect ratio on the effective mechanical properties. Furthermore, we highlight the importance of tunneling resistance on the electrical conductivity and discuss the key parameters that influence percolation behavior in the said nanocomposite.

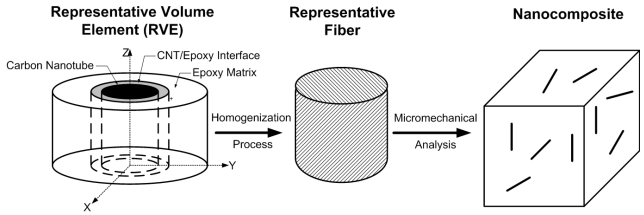

Figure 1: Schematic illustration of mechanical analysis procedure.

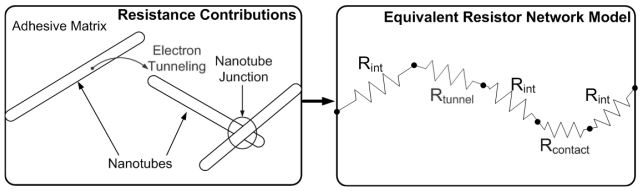

Figure 2: Equivalent resistor network model.

2 ATOMISTIC-BASED CONTINUUM MODELING

A three-dimensional nonlinear RVE is developed to study the nano-reinforced epoxy system. The RVE consists of the reinforcing CNT, the surrounding polymer matrix, and the CNT-epoxy interface, as depicted in Figure 3. Due to the inherent nano-scale involved in simulating CNT structures, an atomistic description is incorporated. First, the covalent bonds in the CNT structure are described using the Modified Morse interatomic potential. Secondly, the atomic vdW interactions between the atoms in the CNT and

the atoms in the epoxy matrix are described using the Lennard-Jones (LJ) interatomic potential. This description implies the assumption of a non-bonded interfacial region.

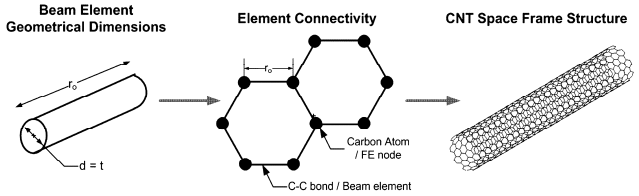

Figure 3: Carbon nanotube spaceframe structure.

The CNT is modeled as a space-frame structure as depicted in Fig. 2. In the space-frame model, each beam element corresponds to an individual chemical bond in the CNT. As in traditional FE models, nodes are used to connect the beam elements to form the CNT structure. In this case, the nodes represent the carbon atoms and their positions are defined by the same atomic coordinates. We adopt the Modified Morse potential with an added angle-bending potential to describe the atomic interactions in the CNT. This potential is given by:

$$E = E_s + E_b \tag{1}$$

$$E_s = D_e\left(\left[1-\exp^{-\beta(r-ro)}\right]^2 - 1\right) \tag{2}$$

$$E_b = \frac{1}{2}k_\theta\left(\theta-\theta_o\right)^2\left[1+k_{sextic}\left(\theta-\theta_o\right)^4\right] \tag{3}$$

where r_o is the initial bond length, θ_o is the initial angle between adjacent bonds, D_e is the dissociation energy, β is a constant which controls the 'width' of the potential, and k_θ and k_{sextic} are the angle-bending force constants. Nonlinear rotational spring elements are used to account for the angle-bending component, while beam elements are used to represent the stretching component of the potential.

The Lennard-Jones interatomic potential is used to describe the vdWs interactions at the CNT/polymer interface. The LJ potential is defined as

$$E_{LJ} = 4\mu\left[\left(\frac{\psi}{r}\right)^{12} - \left(\frac{\psi}{r}\right)^{6}\right] \tag{4}$$

where μ is the potential well depth, ψ is the hard sphere radius of the atom or the distance at which E_{LJ} is zero, and r is the distance between the two atoms. Differentiating the potential with respect to the separation distance, we arrive at an expression for the vdW force between two interacting atoms

$$\mathrm{F_{LJ}} = 24\left(\frac{\mu}{\psi}\right)\left[2\left(\frac{\psi}{\mathrm{r}}\right)^{13} - \left(\frac{\psi}{\mathrm{r}}\right)^{7}\right] \tag{5}$$

This expression is used to determine the magnitude of the force in each interaction, which depends solely on the separation distance between the atoms and the type of atoms considered.

To model the surrounding epoxy matrix, a specific two-component epoxy structural adhesive is used based on a DGEBA / TETA formulation. This adhesive is a virgin epoxy with no added fillers. Tension tests according to ASTM D638 were conducted on cured dogbone test specimens to determine the average constitutive response of the cured adhesive. The measured stress-strain response is used to characterise the surrounding homogeneous and continuous solid matrix phase.

To address the scale-up to the macro level, the RVE is homogenized into a representative fiber exhibiting the same geometrical and mechanical characteristics such that it behaves as an equivalent continuous medium. The mechanical properties of the representative fiber are determined by evaluating the nonlinear constitutive response of the RVE subject to a tensile load. The fiber is in turn used to describe the reinforcing phase in large scale 3D FEA-assisted nonlinear micromechanical to provide an estimate of the nonlinear mechanical properties of the nanocomposite for varied CNT concentrations. In this way, the representative fiber acts as a vital link between atomistic and continuum scales. Figure 4 depicts one such model for the case of 0.5wt% CNT concentrtation and aspect ratio 100.

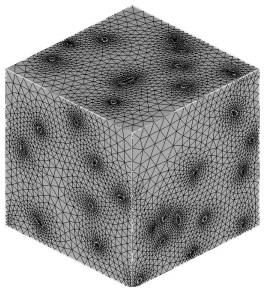

Figure 4: Computational cell used in FEA-assisted nonlinear micromechanical modeling.

3 EQUIVALENT RESISTOR NETWORK MODELING

A novel three-dimensional random percolation model is set up to investigate the electrical conductivity of the nanocomposites.

In most previous works, the percolation threshold and the electrical conductivity were evaluated by recognizing the connective percolating network linking two opposite faces of a single representative cuboid volume (grey dashed lines in Fig. 5(a)). Following the methodology of these earlier works, the electrical current cannot always propagate periodically (cf. grey dashed lines in Fig. 5(a) and 5(b)), although periodic boundary conditions for CNT configurations were enforced. To eliminate these unexpected anomalies, we developed an improved network recognition approach. In our novel approach, the continuity of the network is ensured by introducing periodically connective paths. The light grey solid lines in Fig. 5(a) and 5(b) show this idea in a 2-D plot. In our investigation, this technique was generalized to the 3-D network and proven

to effectively reduce the finite-size effect of the representative volume. Furthermore, we incorporated Landauer-Büttiker formula (Eq. 6) to evaluate the resistance between two CNTs contacting at the mesoscopic scale. With these techniques applied in our Monte Carlo simulations, we were able to fully analyze the electrical conductivity of nanocomposites containing uniformly distributed, aligned and agglomerated CNTs.

$$R_{\text{int}} = h / 2e^2 MT \qquad (6)$$

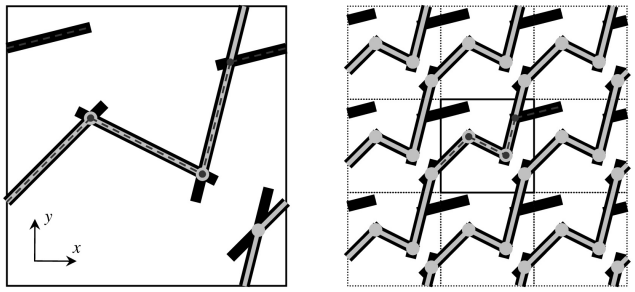

Figure 5: Schematic diagrams of percolating paths (grey dashed lines and light grey solid lines) recognition among periodically distributed CNTs (black lines) with different viewpoints: The grey dashed lines in (a) denote the network consists of paths simply linking two boundaries; This network cannot conduct a periodic current flow as shown in (b); The light grey solid lines in (a) denote the network developed in terms of periodically connective paths. Current flow can periodically transport in this network as shown in (b).

4 RESULTS AND DISCUSSION

As an intermediary step in the study of the effective mechanical properties of nano-reinforced composites, the nonlinear response of individual CNTs was investigated. Two CNT arrangements were studied: the (16,0) zigzag nanotube and the (9,9) armchair nanotube, both having diameters of approximately 1.2 nm and lengths of 10 nm. Two loading conditions were investigated to obtain both tensile and shear properties.

The results show that the zigzag nanotube can withstand a strain of 17%, while the armchair nanotube can withstand a strain of up to 22% in tnesion. The respective tensile modulus for the armchair and zigzag nanotubes are 944.8 GPa and 920.2 GPa. The overall trend of the stress-strain curves agree well with others in the literature [1,2], and also show that the armchair configuration exhibits higher strength and stiffness when compared to the zigzag configuration as shown in Fig. 6.

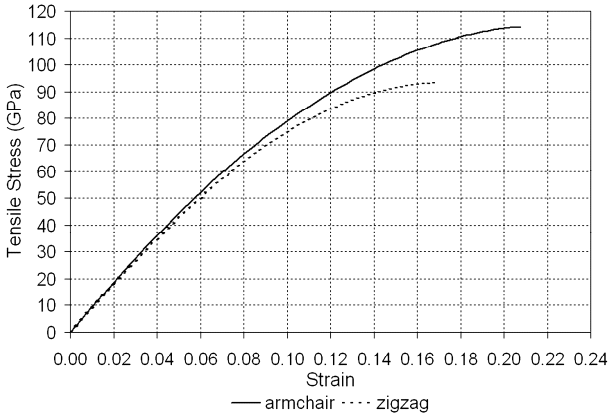

Figure 6: Tensile stress-strain curves for zigzag and armchair nanotubes

By equating the associated strain energies under identical loading conditions, we were able to homogenize the RVE into a representative fiber. The homogenized RVE was then employed in a Mori-Tanaka based micromechanical analysis to predict the effective properties of the newly developed nanocomposite. Numerical examples show that the effect of volume fraction, orientation, and aspect ratio of the CNTs on the properties of the nanocomposite can be significant. For example, Fig. 7 shows the effect of CNT volume fraction on the longitudinal Youngs modulus for both aligned and randomly oriented CNTs.

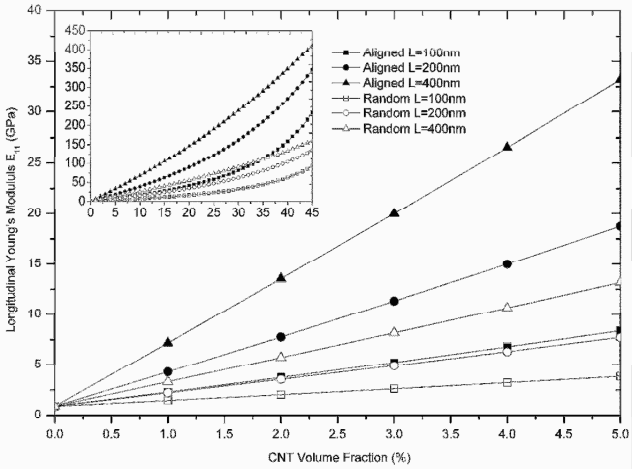

Figure 7: Effect of CNT volume fraction on the longitudinal Young's modulus.

The representative fiber was also used to model the reinforcing phase in large scale FEA-assisted nonlinear micromechanical models. The resulting mechanical property predictions show good agreement with experimental measurements as shown in Fig. 8 for the case of 0.5wt% CNT concentration.

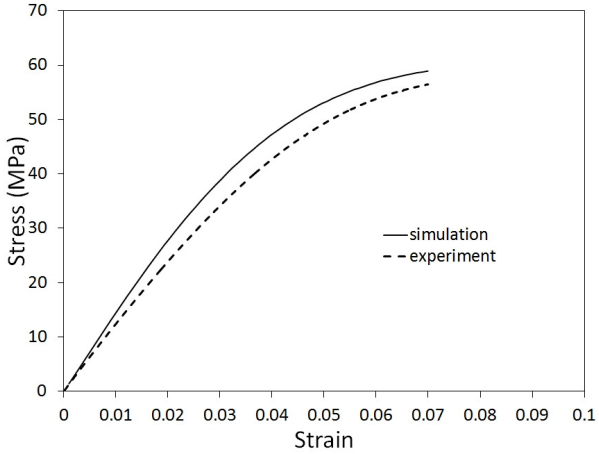

Figure 8: Constitutive response of bulk nanocomposite.

Furthermore, we compared the numerical results of our random network model with various experiments. In Fig. 9, our numerical predictions for uniformly distributed MWCNTs show good agreement with experimental results [3]. Our model predicts that the critical percolation threshold is around 1% volume fraction.

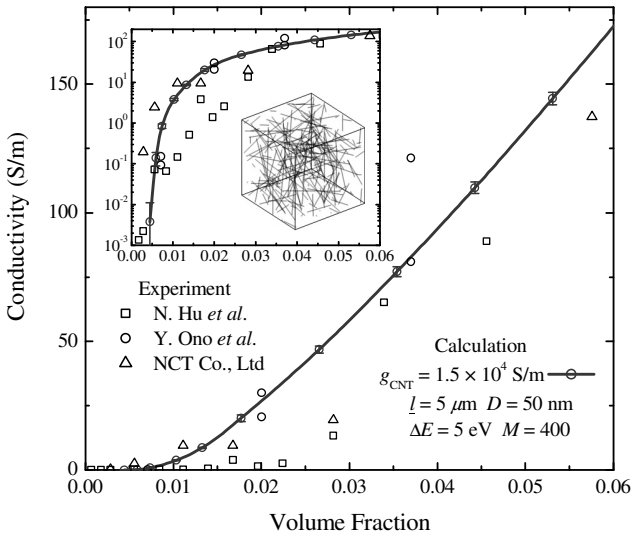

Figure 9: Comparison of predicted electrical conductivity with existing experimental data.

In Fig. 10, our theoretical model is also used to make a quantitative comparison with Du *et al*'s experimental data [4] for SWCNTs. In Du *et al*'s work, the degrees of CNT alignment satisfy the Lorentz distribution which is characterized by the full width at half maximum (FWHM). In our calculations, we approximate the Lorentz function as being uniform in the range $[-\theta_{\max}, \theta_{\max}]$, and obtain the relationship $\mathrm{FWHM} = 2\theta_{\max}$. Whenever the original data are given in terms of weight fraction (wt%), we converted them to volume fraction (vol%) by the relationship wt% = vol% for SWCNTs. It is shown in Fig. 9 that if we choose $\sigma_{\mathrm{CNT}} = 1\times10^{2}$ S/m, the numerical results agree well with the experimental data of Du *et al* [4] for the 2% and 3% volume fractions.

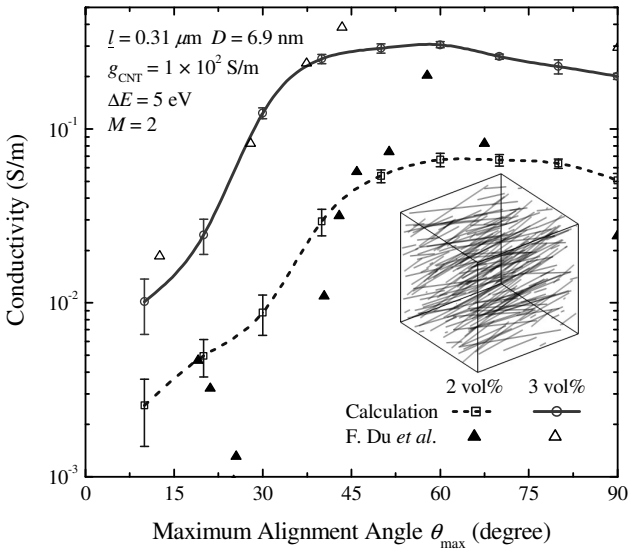

Figure 10: Comparison of predicted alignment effects of CNTs with existing experimental findings.

5 FUTURE WORK

As an extension of the current numerical work the electrical footprint of common damage phenomena will be investigated. Here the ABC and resistor network models will integrated into a unified model. In this way we hope to demonstrate the potential to use CNTs networks as sensors of in situ local damage of structural adhesive bonds.

REFERENCES

[1] T. Belytschko, S.P. Xiao, G.C. Schatz, R.S. Ruoff, Physical Review B 65, 1-8, 2002.
[2] J.R. Xiao, J. Staniszewski, J.W. Gillespie Jr., Composite structures 88, 602-609, 2009.
[3] N. Hu, Z. Masuda, G. Yamamoto, H. Fukunaga, T. Hashida, and J. Qiu, Composites Part A: Applied Science and Manufacturing 39, 893, 2008.
[4]. F. Du, J. E. Fischer, and K. I. Winey, Physical Review B 72, 121404, 2005.